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X-ray standing wave studies of the structural properties of ion beam synthesized epitaxial $Si/CoSi_2/Si(111)$ system

P V Satyam and B N Dev
Institute of Physics, Sachivalaya Marg, Bhubaneswar-751 005, Orissa, India

Abstract : The atomic structure of the (111) interface between ion beam synthesized buried $CoSi_2$ epilayer (type-A) and bulk Si has been investigated by using bulk X-ray diffraction and X-ray standing waves. Our results show that the $CoSi_2$ lattice is 0.7% contracted in the [111] direction compared with the $CoSi_2$ bulk lattice constant. At the interface, the Co atoms of the $CoSi_2$ epilayer are directly bonded to the interfacial Si atoms of the bulk Si(111) substrate conforming to the 8-fold Co coordination model. The Co–Si bonds at the interface are contracted by 0.04 ± 0.06 Å with respect to that in bulk $CoSi_2$.

Keywords : X-ray standing waves, X-ray diffraction, ion beam synthesis, epitaxial $Si/CoSi_2/Si$.

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1. Introduction

Heterostructures formed by growing epitaxial metallic silicides, such as $NiSi_2$ and $CoSi_2$, on silicon substrates are of considerable interest because of their fundamental importance and possible technological applications. An understanding of the basic aspects of atomic bonding geometry and the electronic properties at the interfaces of the heteroepitaxial structures contribute to their effective use in microelectronic applications. The nearly lattice matched $NiSi_2/Si(111)$ and $CoSi_2/Si(111)$ systems have been studied by various experimental [1–7] and theoretical techniques [8–10] leading to an understanding of these interfaces. Conventionally the epitaxial metallic silicide layers are grown on Si surfaces under ultrahigh vacuum (UHV) condition by Solid Phase Epitaxy (SPE), Molecular Beam Epitaxy (MBE) and Reactive Deposition Epitaxy (RPE). White *et al* [11] used high-does ion implantation into silicon substrates, followed by annealing, to grow buried epitaxial layers. This method is known as Ion Beam Synthesis (IBS). The epitaxial silicide layers grow in two possible orientations : type-A, where the silicide layer has the same orientation as the Si substrate, and

type-B, where the silicide layer is rotated 180° about the surface normal of the Si substrate [12]. The IBS prepared silicides have received much attention as the electrical transport properties of epitaxial $CoSi_2$ layers formed by IBS are better than those formed by the conventional UHV procedure and the possible application of an IBS-fabricated $Si/CoSi_2/Si$ heterostructure as a metal base transistor [13,14].

A complete understanding of electronic properties of the epitaxial silicide layers requires detailed knowledge of atomic bonding configuration at the interface. Possible models for both A-type and B-type have been proposed by Cherns *et al* [2]. Either the metal atoms or the Si atoms of the silicide can be bonded to the substrate, leading to either an 8-(or 5-) or 7-fold coordination of the interfacial metal atoms (Figure 1). The 8-fold coordination model comprises an extra plane of Si atoms at the interface on silicide-lattice positions compared to

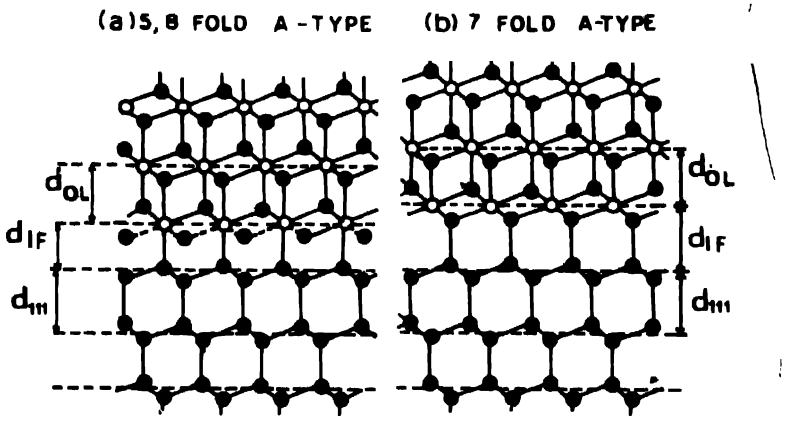

Figure 1. Possible models of the $CoSi_2/Si(111)$ interface for the type-A structure. Open and filled circles represent Co and Si atoms, respectively. The Co atoms are 5-fold coordinated (a) when the extra plane of Si atoms at the interface is absent

the 5-fold coordination model. Earlier experiments by Gibson *et al* using high resolution electron microscopy (HREM) on B-type $CoSi_2/Si(111)$ samples, prepared by Co deposition on Si(111) substrates and annealing under UHV conditions, showed the evidence for 5-fold coordinated interface structure [1]. But recently Catana *et al* used the same UHV deposition and annealing technique to obtain both B-type and A-type $CoSi_2/Si(111)$ interfaces, and using the same technique (HREM) they observed sevenfold (as well as some eightfold) coordination for the B-type $CoSi_2/Si(111)$ samples [15], which contradicts the observations of Gibson *et al*. Other techniques such as X-ray standing wave (XSW) [4,5] and high resolution Rutherford backscattering spectrometry (RBS) [6] found the interface of B-type $CoSi_2/Si(111)$ to be 5-fold coordinated, supporting the observations of Gibson *et al*. Catana *et al* found evidence for the sevenfold coordination for the A-type interfaces as well. Bulle-Lieuwma *et al* carried out HREM studies on the IBS-prepared A-type $CoSi_2/Si(111)$ interface in the $Si/CoSi_2/Si$ samples and their results favour a 7-fold interface model [16]. Theoretical calculations, such as local-density-functional [8] and quantum chemical cluster [9] calculations, however, favour the 8-fold coordination model for both A- and B-type

$CoSi_2$/Si(111) interfaces. Given the contradictions, it is clear that further experimental studies on the $CoSi_2$/Si(111) A-type interface are necessary. In the present work we have undertaken the study of the A-type $CoSi_2$/Si(111) interface in the IBS-prepared Si/$CoSi_2$/Si(111) system with a buried epitaxial $CoSi_2$ layer. We have used the XSW technique to determine the bonding geometry at the interface by generating standing waves with the (111) reflection from the Si substrate crystal and monitoring the Co fluorescence yield from the buried layer as a function of incident angle within the angular range of the (111) reflection from the substrate.

The XSW technique is based on the dynamical theory of X-ray diffraction and is explained in a number of publications [17–21]. Here we will give a brief account of the technique. When a monochromatic X-ray beam is Bragg-reflected from a large perfect crystal substrate, the interference between the incident and the reflected waves gives rise to a standing wave field in the substrate. This field also extends across the interface into the overlayer. The phase ν of the standing wave field changes by π radians as the crystal is rocked through the Bragg reflection. On the low-angle side of the reflectivity curve the antinodal planes of the standing wave field lie half-way between the diffraction planes and move inward with increasing angle of incidence towards a position coinciding with the diffraction planes. The position of the buried layer atoms is determined by measuring the standing wave-excited fluorescence yield from those atoms along with the substrate reflectivity as a function of rocking angle.

Let us consider a buried epitaxial $CoSi_2$ layer to be composed of N lattice planes of the fluorescing element Co with a planar spacing d_{OL} and starting at a distance d_{IF} from the topmost diffraction plane of the substrate (Figure 1). The relevant difference between the 8-fold (or 5-fold) and the 7-fold coordination is in the value of d_{IF}. From the models shown in Figure 1, the value d_{IF} for unrelaxed 7-fold and 8-(or 5-) fold coordinated interfaces is 3.52 Å and 2.74 Å, respectively. We introduce the parameters $\delta_{IF} = d_{IF}/d_H$ and $\gamma = d_{OL}/d_H - 1$ and use the formalism given in ref. [3]. In this case, d_H is the (111) planar spacing in silicon.

The normalized fluorescence yield $Y_F(\theta)$, emitted by N overlayer planes as a function of incident angle θ is given by

$$Y_F(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)}\,F\cos\left[\nu(\theta) - 2\pi\Phi_c\right] \tag{1}$$

where the reflectivity $R(\theta)$ and the phase $\nu(\theta)$ can be calculated from the dynamical theory. Φ_c and F are called coherent position and coherent fraction, respectively. All possible fluorescence yield ($Y_F(\theta)$) curves can be fitted with these two parameters. Φ_c and F are defined as follows [3,7].

$$\Phi_c = \delta_{IF} + (N-1)\gamma/2, \tag{2}$$

$$d_{IF} = \Phi_c d_H - (N-1)\gamma d_H/2, \tag{3}$$

$$F = f_c \sin\left(\pi N_\gamma\right)/N\sin(\pi\gamma). \tag{4}$$

f_c contains the Debye-Waller factor and the information about the crystallinity of the epitaxial layer. γ can be determined from the XSW experiments as was done in ref. [3] or can be determined directly from the angular separation of the X-ray diffraction peaks from the epilayer and the substrate as has been done here. The value of γ or d_{OL} contain the information about the strain in the epilayer. The film thickness is determined by other methods such as RBS. Now with the known values of N and γ, d_{IF} is determined from the measured value of Φ_c from the XSW experiment. This gives the interface structure.

An Si wafer (p-doped) with (111) orientation was implanted with 200 keV Co^+ ions to a dose of $2 \times 10^{17}/cm^2$ while the substrate was kept at 350°C. This was followed by an annealing treatment of one hour at 600° C and 30 minutes at 1000°C to form a 680 ± 50 Å thick A-type epitaxial $CoSi_2$ buried layer under 880 Å of crystalline Si [22]. This sample will be denoted by $Si/CoSi_2/Si(111)$ and is schematically shown in the inset of Figure 3. The method of this preparation of an epilayer is known as ion beam synthesis (IBS).

The X-ray diffraction (XRD) and the XSW measurements were carried out at the Hamburg Synchrotron Radiation Laboratory (HASYLAB), DESY. The experimental arrangement has been described in details elsewhere [23]. With the use of an asymmetrically cut double-crystal monochromator the synchrotron X-radiation from DORIS was collimated and monochromatized to obtain 9.2 keV photons incident on the sample (Figure 2). The Co K_α fluorescence yield was measured with a Si(Li) detector and the reflected X-ray intensity

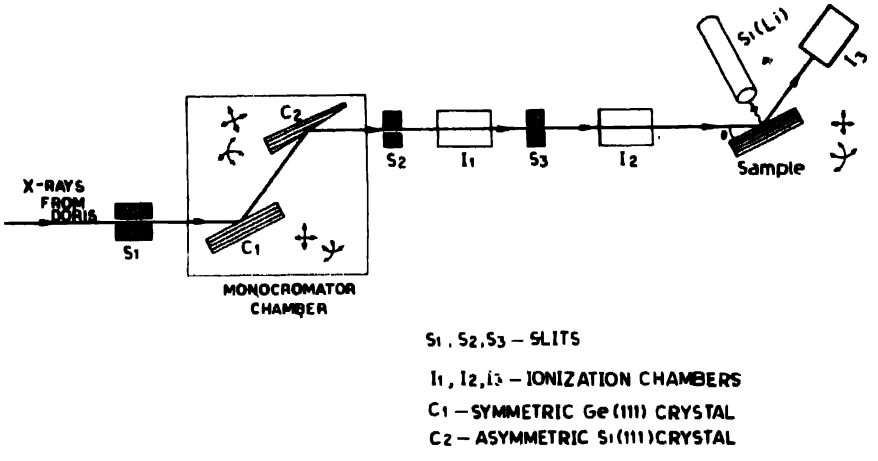

Figure 2. Schematic experimental setup at the ROEMO station, HASYLAB at DESY.

was measured with an ionization chamber (Figure 2). High resolution topograms were taken to select a reasonably perfect crystalline region on the sample for the XSW measurement.

It is well known that the lattice structure of $CoSi_2$ is of the CaF_2 type and the lattice constant is 1.2% smaller than that of Si. That is, the (111) planar spacing in $CoSi_2$ is 3.097 Å. However, for the buried epitaxial $CoSi_2$ layer the (111) planar spacing (*i.e.*, the value of d_{OL}) has been determined to be 3.075 ± 0.0005 Å. This value was determined from the

angular positions of the (111) diffraction peaks from the substrate Si and the $CoSi_2$ epilayer (Figure 3). The measured value of d_{OL} corresponds to a perpendicular strain in the buried

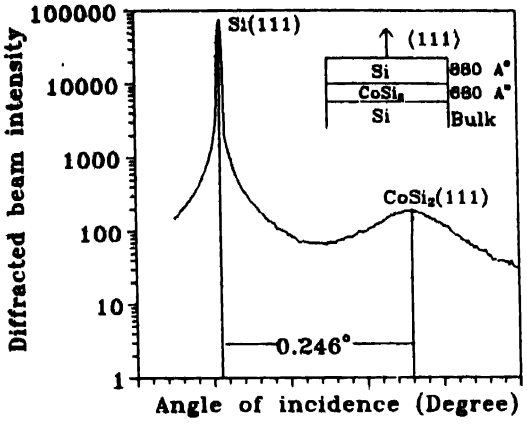

Figure 3. Bulk X-ray diffraction peaks obtained from the sample when scanned by varying the angle of incidence θ in steps of 0.002°. The sample is schematically shown in the inset.

$CoSi_2$ layer of – 0.71% with respect to the $CoSi_2$ bulk lattice constant. This corresponds to $\gamma = -1.93 \times 10^{-2}$, whereas a pseudomorphic growth would correspond to $\gamma = -2.30 \times 10^{-2}$. For a complete absence of strain, that is with the $CoSi_2$ bulk lattice parameter, $\gamma = -1.20 \times 10^{-2}$. Our measured value of $\gamma = -1.93 \times 10^{-2}$ is in good agreement with those measured by Vantomme *et al* [24] for IBS-prepared $CoSi_2$ films of thicknesses in the range 100–600 Å.

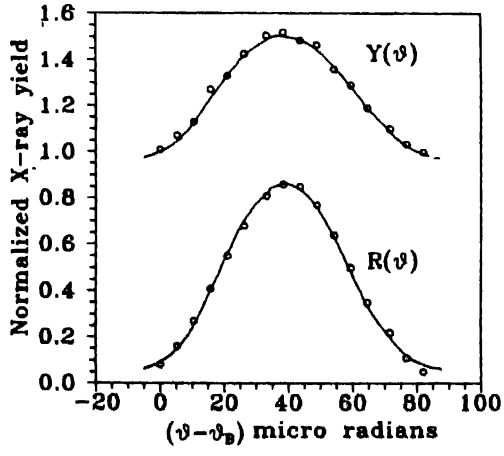

Figure 4. $R(\theta)$ and $Y(\theta)$ are the Si substrate reflectivity and the Co K_α fluorescence yield, respectively.
Circles : experiment; Lines : best fit to the XSW theory. The fit gives $\Phi_c = 0.756 \pm 0.01$ and $F = 0.15 \pm 0.05$. The error bars are included in the size of the circles.

With the known film thickness and the measured value of d_{OL}, the number of $CoSi_2$ layers N is determined. The values of N and γ are 221 ± 16 and –0.0193 ± 0.0005, respectively. The

results of the XSW experiment, namely, the Si(111) reflectivity $R(\theta)$, and the Co K_α fluorescence yield $Y_F(\theta)$ with the corresponding fit are shown in Figure 4. The parameters Φ_c and F have been obtained by fitting the theoretical yield function to the experimental Co fluorescence yield. The values are $\Phi_c = 0.756 \pm 0.01$ and $F = 0.15 \pm 0.05$. From eq. (3) d_{IF}(expt) = 2.67 ± 0.06 Å.

From the models shown in Figure 1, ignoring the small difference in bond length between Si–Si and Co–Si, and taking them to be equal to the bulk Si–Si bond length (2.35 Å), the value of d_{IF} expected for the 7-fold coordination is 3.52 Å and that for 8- (or 5-) fold coordination is 2.74 Å. Figure 5 shows the computed coherent position and coherent

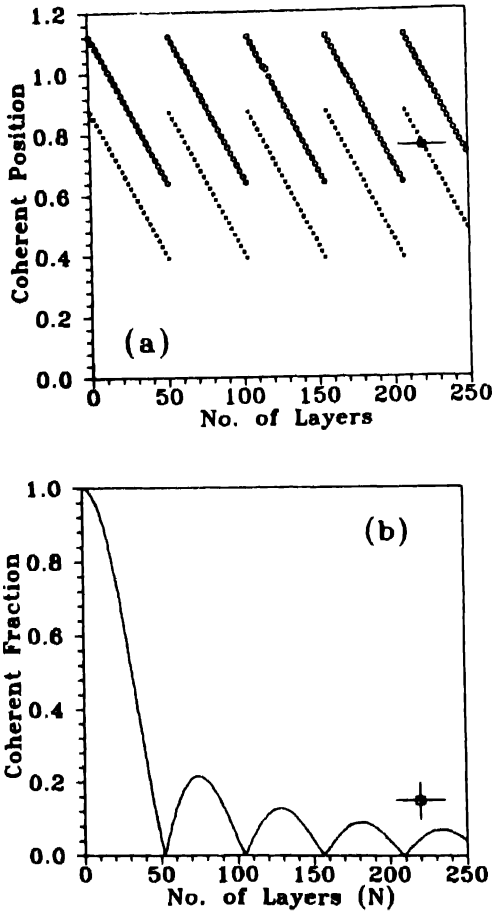

Figure 5. (a) Coherent position (Φ_c) and (b) coherent fraction (F) computed from the number of Co layers (N) and the experimentally determined strain (γ) for different interface models. Asterisks and circles represent the computed coherent position for the 8-(or 5-) fold and the 7-fold model, respectively. Measured values are shown by squares.

fraction for the 8-(or 5-) fold and the 7-fold coordination of Co at the interface and the experimental values of Φ_c and F. It is clear that our experimentally determined Φ_c, and

consequently d_{IF}, is in good agreement with the 8-(or 5-) fold model and we can rule out the 7-fold model. In order words, the Co atoms of the $CoSi_2$ layer are directly bonded to the surface Si atoms of the substrate. It should be noted that this analysis refers to the $CoSi_2$/ bulk Si interface (see the inset of Figure 3). The difference $\Delta d_{IF} = d_{IF}(\text{expt}) - d_{IF}(\text{8-fold}) = -0.07$ Å. This value would actually correspond to an interface Si–Co bond length of 2.28 ± 0.06 Å, if the substrate surface Si atoms are at their ideal position. Since the Co–Si bond length in bulk $CoSi_2$ is 2.32 Å, the measured value represents a 0.04 ± 0.06 Å contraction of the interface Co–Si bond. In previous XSW measurements on epitaxially grown B-type $CoSi_2$ on Si(111) surface it was concluded that the Co atoms at the interface are five-fold coordinated. In the XSW measurement fivefold coordination cannot be distinguished from the eightfold one as both the models would give practically the same d_{IF}. Recent local-density-functional (LDF) [8] and quantum chemical cluster [9] calculations showed that the eightfold coordination, for both B- and A-type, is much more favourable than the fivefold coordination. So, the 8-fold coordination for the B-type interface appears to be established. In the two sets of previous XSW measurements on B-type $CoSi_2$/Si(111) samples it was observed that the Co atoms at the interface are relaxed outward by 0.05 ± 0.03 Å and 0.14 ± 0.05 Å for films in the ranges 3–9 [4] and 20–51 Co layers [5], respectively. Here we observe for the A-type $CoSi_2$ film containing 221 Co layers 0.04 Å ± 0.06 Å contraction of the interface Co–Si bond in comparison with the bulk Co–Si bond length. Whether this difference in the relaxation is due to the additional epitaxial Si layer on top of the buried $CoSi_2$ layer or because the film is A-type is not clear. The difference in the relaxation for the 8-fold A- and the 8-fold B-type interfaces may lie in the fact that the A-type interface has an overcoordinated Si atom whereas the B-type interface has an undercoordinated Si atom. Indeed, a perusal of the contour plots of the constant valence charge density obtained from the LDF theory [25] for the 8-fold A, 8-fold B and bulk $CoSi_2$ shows that the Si–Co bond at the A-type interface is stronger compared to both the B-type interface and bulk $CoSi_2$. This may be responsible for the Si–Co bond length contraction at the A-type interface. A difference in the relaxation for the A- and B- type interfaces was also observed for the $NiSi_2$/Si(111) system [3,7].

The measured coherent fraction in the present experiment is higher than the theoretical value. One notices this trend for large film thicknesses. Zegenhagen *et al* [7] studied $NiSi_2$ epilayer on Si(111) with film thickness in the range 63–976 Å (20–314 Ni layers). There one notices that the measured coherent fraction falls below the theoretical value for thin layers and above for thick layers. For larger thicknesses the assumption of a constant planar spacing (d_{OL}) may need to be modified. In fact, the measured full width at half maximum (FWHM) of the (111) diffraction peak from the $CoSi_2$ layer is more than what is expected from a perfect 680 Å $CoSi_2$ layer with uniform (111) planar spacing [26]. However, this minor modification is not expected to change the conclusion regarding d_{IF} and the interface coordination.

For the study of the B-type $CoSi_2$/Si(111) system high resolution electron microscopy (HREM) was used by Gibson *et al* [1]. As a definite structure-assignment may be hampered by the uncertainties in the HREM image simulation parameters, they identified the 5-fold coordination of the interface Co atoms as the most likely model. This was later on supported by XSW [4,5] and ion scattering [6] studies. However, using the HREM technique Catana *et al* [15] obtained evidence for 7-fold (in some cases eightfold) coordination for the B-type interface, which contradicts even the previous HREM studies. For the A-type interface as well they showed evidence for sevenfold coordination. In both the HREM studies [1,15] the sample preparation procedures were essentially the same—by room temperature Co deposition on Si and annealing under UHV condition. On the IBS-prepared Si/$CoSi_2$/Si(111) systems, there were HREM studies by Bulle-Lieuwma *et al* [16] on both A- and B- type $CoSi_2$/Si(111) interfaces. Through the computer simulations of the HREM images the obtained evidence for eightfold coordination of the B-type and sevenfold coordination of t A-type interface. It should be noted that theoretical calculations show the lowest interface energy for the eightfold B-type interface. For the A-type interface the sevenfold configuration has 26% (~ 0.2 eV) higher interface energy compared to the eightfold configuration [8,28], making the latter more likely. This agrees with our observations.

One point needs to be discussed here. The present work is the first XSW measurement on an A-type $CoSi_2$ layer on silicon. In fact, except for two HREM studies [15,16], all the other works on $CoSi_2$/Si were on B-type samples. From the XSW primary analysis one gets a coherent position and a coherent fraction and one would feel uncomfortable to carry on further analysis when the measured coherent fraction is low. In the present work the measured coherent fraction is small (0.15 ± 0.05). However, there is a constraint for the IBS-prepared buried A-type $CoSi_2$ layer. In the case of Si(111) substrate it has not been possible to prepare pure A-type $CoSi_2$ layer for a film thickness less than 300 Å (97 Co atomic layers) [16]. Layers of thicknesses below this critical value are mixed A- and B-type. For example, a 360 Å (117 atomic layers) $CoSi_2$ buried film is 100% A-type, a 240 Å (78 layers) film is 87% A-type and films of smaller thicknesses have a decreasing percentage of the A-type constituent [25]. Taking the possible thickness of a pure A-type IBS-prepared $CoSi_2$ buried layer to be $\geq$ 300 Å (97 atomic layers), we notice from Figure 5(b) that the maximum coherent fraction one would get from an A-type layer is about 0.15. It may be possible to remove the top Si layer and a part of the $CoSi_2$ layer by controlled etching leaving only thin A-type $CoSi_2$ overlayer. As seen in Figure 5(b), a thickness of $\leq$ 30 Co atomic layers would be necessary to give a coherent fraction of $\geq$ 0.5. However, this thinning process may affect the epilayer characteristics, if not the interfacial structure.

In conclusion, we have made X-ray diffraction and X-ray standing wave measurements on buried $CoSi_2$ layer in the Si(880 Å)/$CoSi_2$(680 Å)/Si(111) system prepared by Ion Beam Synthesis, namely, Co ion implantation into Si(111) and subsequent annealing. The $CoSi_2$ layer was A-type. The (111) planar spacing and the strain in the $CoSi_2$ were determined with high resolution X-ray diffraction measurements. These values were used in

further XSW analyses leading to the atomic structure of the $CoSi_2$/Si(111) substrate interface. We have found evidence for the eightfold coordination of the Co atoms at the interface, which means that the Co atoms of the silicide layer are directly bonded to the surface Si atoms of the substrate. The positions of the interface Co atoms are slightly relaxed towards the substrate. Assuming the substrate Si atoms to be at their ideal positions the inward relaxation corresponds to a Co–Si bond length of 2.28 ± 0.06 Å *i.e.*, 0.04 Å shorter than that in bulk $CoSi_2$. It was not possible to determine the structure of the upper Si/$CoSi_2$ interface in the present study. However, knowledge of this interface structure would provide an insight into the growth process of the ion beam synthesized epilayer and the critical thickness for the B → A-type growth.

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